

Supporting Information

L-Glutamic acid derived PtPd@Pt core/satellite nanoassemblies as an effectively cathodic electrocatalyst

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Experimental section

Materials: L-glutamic acid was purchased from Shanghai Kayon Biological Technology CO. Ltd. (Shanghai, China). Poly(vinyl pyrrolidone) (PVP-K30, MW=30,000), palladium chloride (PdCl₂) and chloroplatinic acid hexahydrate (H₂PtCl₆•6H₂O) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Commercial Pt black was purchased from Johnson Matthey Corporation. All reagents were of analytical reagent grade and used as received without further purification.

Synthesis of the PtPd@Pt core/satellite nanoassemblies: In a typical synthesis, 80 mg of L-glutamic acid, 220 mg of PVP, 0.5 ml of PdCl₂ solution (50 mM), 1.5 ml of H₂PtCl₆ aqueous solution (50 mM) were mixed with 9.0 mL of deionized water and stirred for 5 min. The resulting homogeneous solution was transferred to a 15 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 2 h. After being cooled to room temperature, the obtained product (i.e., PtPd@Pt core/satellite nanoassemblies) was separated by centrifugation at 18000 rpm for 20 min, washed three times with deionized water and ethanol, and then dried at 60 °C for 4 h in a vacuum dryer.

Electrochemical measurements: All electrochemical tests were performed on a CHI 760D electrochemical analyzer (Shanghai, Chenghua Co.) equipped with high-speed rotators from Gamry Instruments. A conventional three-electrode system was used, including a rotating disk electrode (RDE) or rotating ring-disk electrode (RRDE) as the working electrodes (0.196 cm²), a Pt wire as the auxiliary electrode, and an Ag/AgCl (1M NaCl) electrode as the reference electrode. All potentials are reported versus the reversible hydrogen electrode (RHE), and for conversion of the obtained potential (vs. Ag/AgCl) to RHE, the following equation was used: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0592 \text{ pH} + E_{\text{Ag/AgCl}}^0$; { $E_{\text{Ag/AgCl}}^0$ (in 1 M KCl) = +0.235 V; pH = 12.9 for 0.1 M KOH}.

Prior to the electrode preparation, the samples were treated with UV irradiation (wavelength at 185

and 254 nm in air for 4 h) to remove the capping agent.^{1, 2} Electrodes were prepared by drop-casting ink containing catalyst powder on a glassy carbon electrode. Typically, 5 mg of the electrocatalyst sample was sonicated in a mixture of 0.9 ml ethyl alcohol and 0.1 ml neutralized Nafion (5 wt%, Sigma-Aldrich) for 30 min to form a homogeneous catalyst ink. The catalyst ink was then coated onto the RDE or RRDE at a loading of 5 μ l and dried at room temperature (loading density of ≈ 0.13 mg cm^{-2}). Cyclic voltammetry (CV) measurements were conducted in N_2 -saturated 0.1 M KOH solution. The ECSA of catalyst was calculated from CVs in 0.5 M H_2SO_4 solution by measuring the charge collected in the hydrogen adsorption/desorption region after double-layer correction and assuming a value of 0.21 mC cm^{-2} for the adsorption of a hydrogen monolayer. For CO-stripping measurements, the catalyst surface was firstly saturated with CO by bubbling CO through a 0.5 M H_2SO_4 solution while holding the working electrode at 0 V for 15 min. The remaining CO was purged by flowing N_2 for 30 min before measurements were made.

The oxygen reduction reaction (ORR) activities of catalysts were measured via the RDE voltammograms in 0.1 M KOH electrolyte at predefined rotation rates and a scan rate of 5 mV s^{-1} . Pure oxygen gas (99.9%) was purged for 30 min before each RDE experiment to make the electrolyte saturated with oxygen. For the RRDE measurements, catalyst inks and electrodes were prepared by the same method as for RDE. The disk electrode was scanned at a rate of 5 mV s^{-1} , and the ring potential was constant at 1.3 V vs RHE. The percentage of HO_2^- intermediate production ($\%\text{HO}_2^-$) and electron transfer number (n) were determined by the followed equations:³⁻⁵

$$\%\text{HO}_2^- = \frac{200I_r}{NI_d + I_r} \quad n = \frac{4NI_d}{NI_d + I_r}$$

where I_d is the disk current, I_r is the ring current, and N is the current collection efficiency of the Pt ring, which was determined to be 0.37.

For the accelerated durability tests, we performed CVs and ORR polarization curves after sweeping 1000 cycles at a rate of 100 mV s^{-1} in an O_2 -saturated 0.1 M KOH solution. Meanwhile, full-scale voltammogram between 0.0 and 1.2 V (vs. RHE) in N_2 -saturated 0.1 M KOH solution were recorded periodically to track the degradation of Pt electro-catalyst.

Instruments: The morphology of the samples were determined by a JEOL JEM-2100F transmission electron microscopy operated at 200 kV , which is used to performing transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area diffraction (SAED), high-angle annular dark-field scanning TEM (HAADF) and energy dispersive X-ray (EDX) elemental mapping measurements. Scanning electron microscopy (SEM) images were taken on a JSM-2010 microscopy at an accelerating voltage of 20 kV . The samples were prepared through dropping the nanocrystal in ethanol dispersions onto carbon-coated Cu grids with a pipette and drying at room temperature. X-ray diffraction (XRD) patterns were recorded on a Model D/max-rC X-ray diffractometer using Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$) and operating at 40 kV and 100 mA . Energy dispersive X-ray (EDX) analysis of particles was carried out on a JSM-2010 SEM. High-resolution X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo VG Scientific ESCALAB 250 spectrometer with an Al K α radiator, and the vacuum in the analysis chamber was maintained at about 10^{-9} mbar . The binding energy was calibrated by means of the C $1s$ peak energy of 284.6 eV . Ultraviolet and visible spectroscopy (UV-vis) spectra were recorded at room temperature on a Shimadzu UV3600 spectrophotometer equipped with 1.0 cm quartz cells.

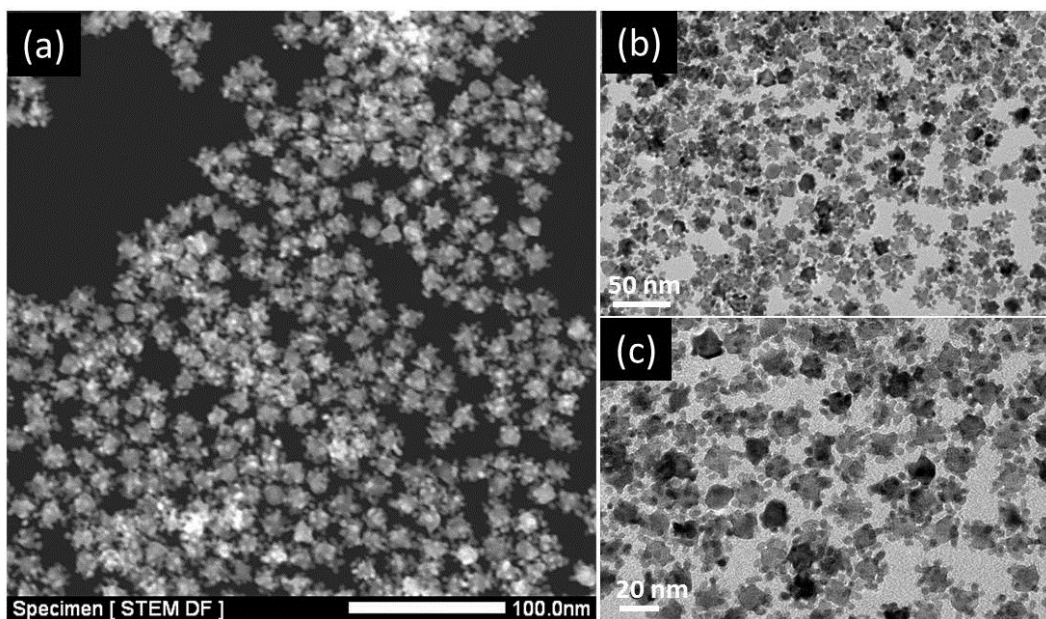


Figure S1. (a) Large-area HAADF-STEM and (b-c) TEM images of the PtPd@Pt core/satellite nanoassemblies.

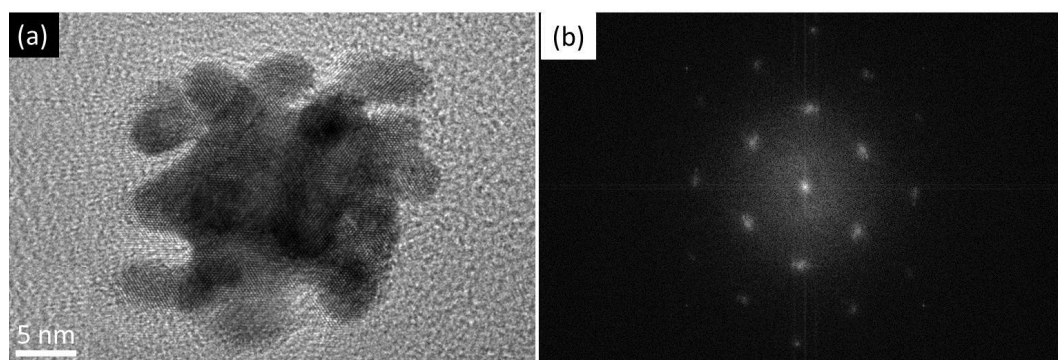


Figure S2. (a) TEM image of a single core/satellite nanoassembly and (b) FFT patterns obtained from (a).

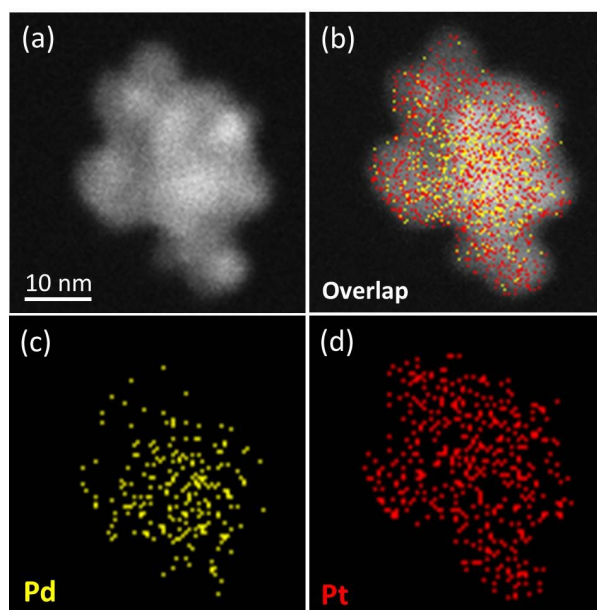


Figure S3. EDX mapping images of the PtPd@Pt core/satellite nanoassemblies.

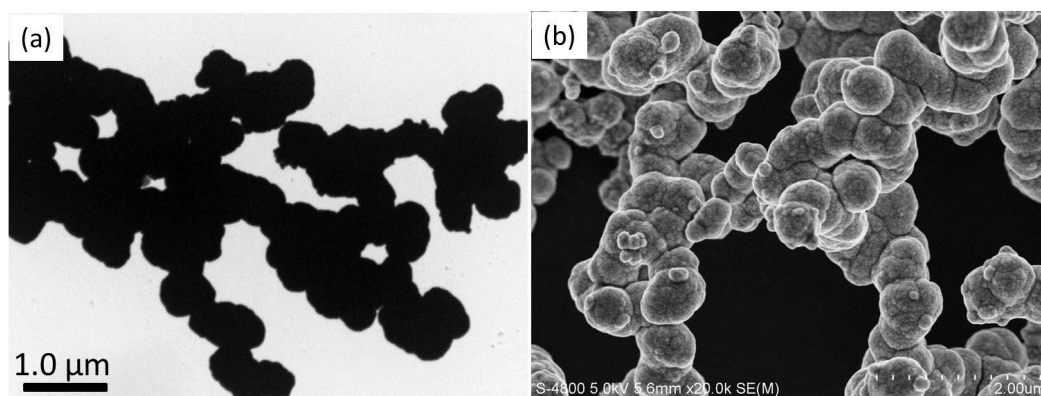


Figure S4. (a) TEM and (b) SEM images of the products prepared using the standard procedure except for the absence of PVP.

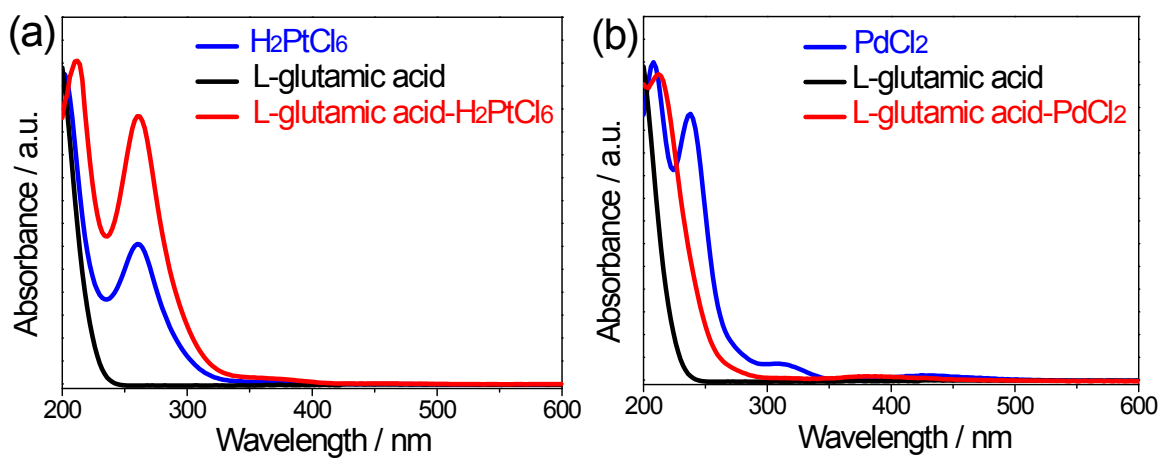


Figure S5. Study of the interactions between the (a) L-glutamic acid and H₂PtCl₆, (b) L-glutamic acid and PdCl₂ by UV-vis spectra at room temperature.

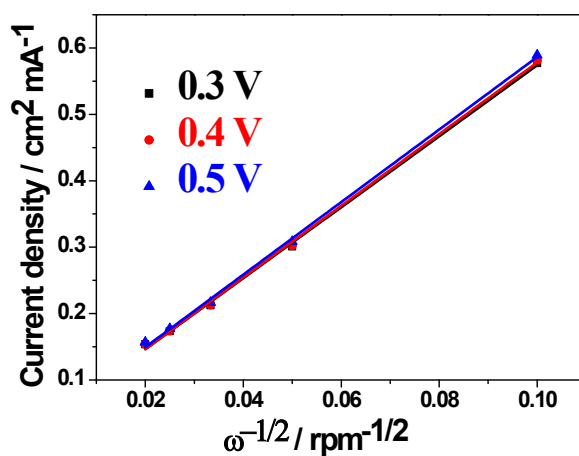


Figure S6. The relevant Koutecky–Levich plots at different potentials.

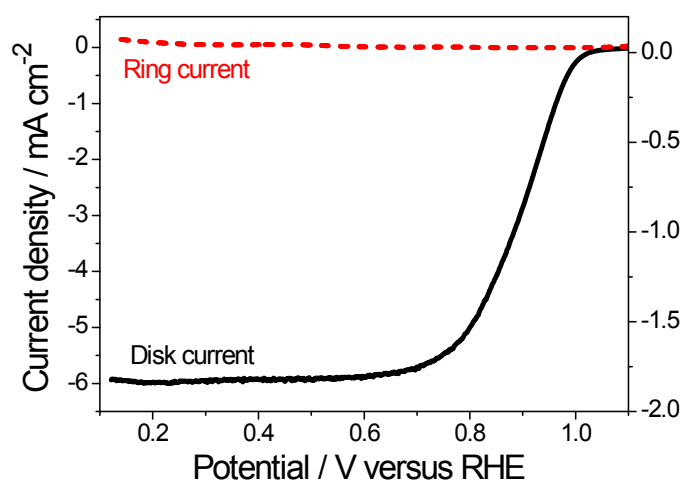


Figure S7. RRDE test of the PtPd@Pt core/satellite nanoassemblies in O₂-saturated 0.1 M KOH solution at a sweep rate of 5 mV s⁻¹ at 1600 rpm.

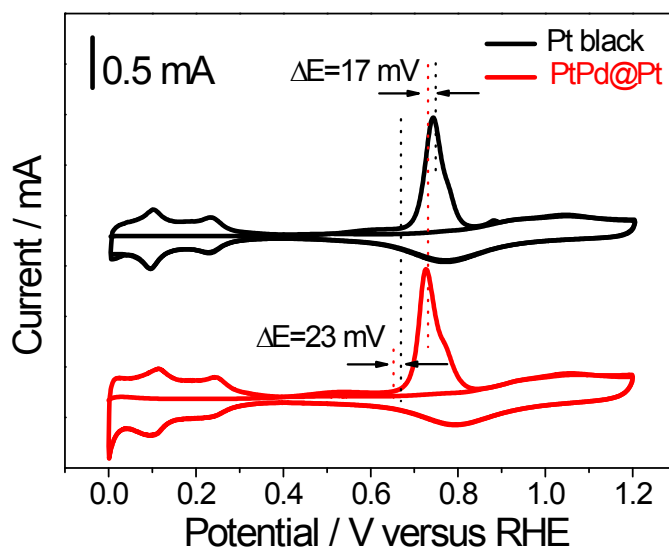


Figure S8. CO stripping curves of the PtPd@Pt core/satellite nanoassemblies and commercial Pt black in N₂-saturated 0.5 M H₂SO₄ solution at 50 mV·s⁻¹.

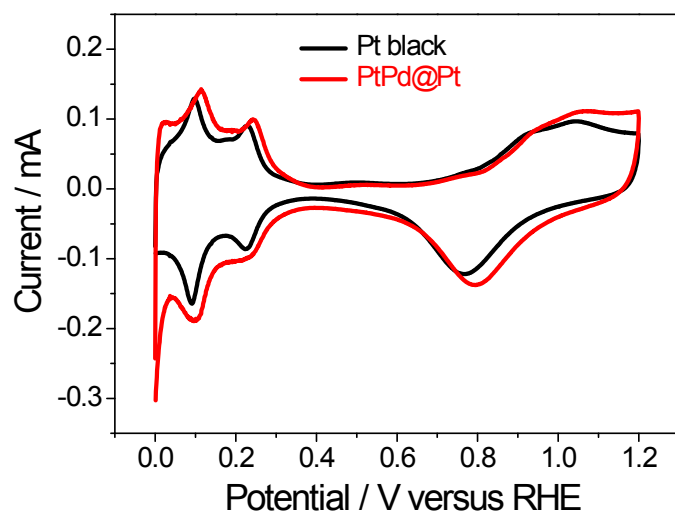


Figure S9. CV curves for the PtPd@Pt core/satellite nanoassemblies and commercial Pt black in N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹.

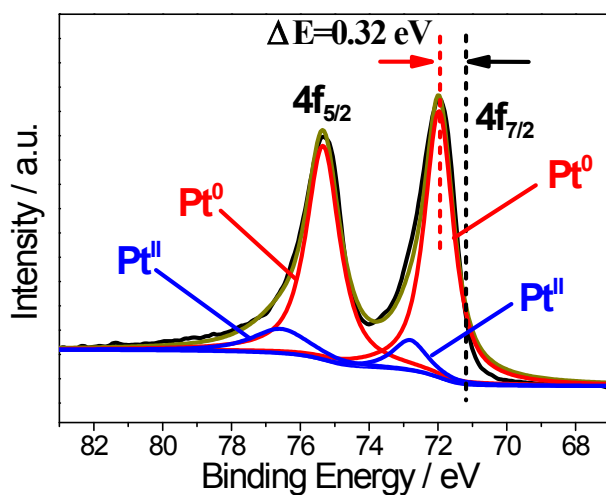


Figure S10. Pt 4f XPS spectrum of the PtPd@Pt core/satellite nanoassemblies.

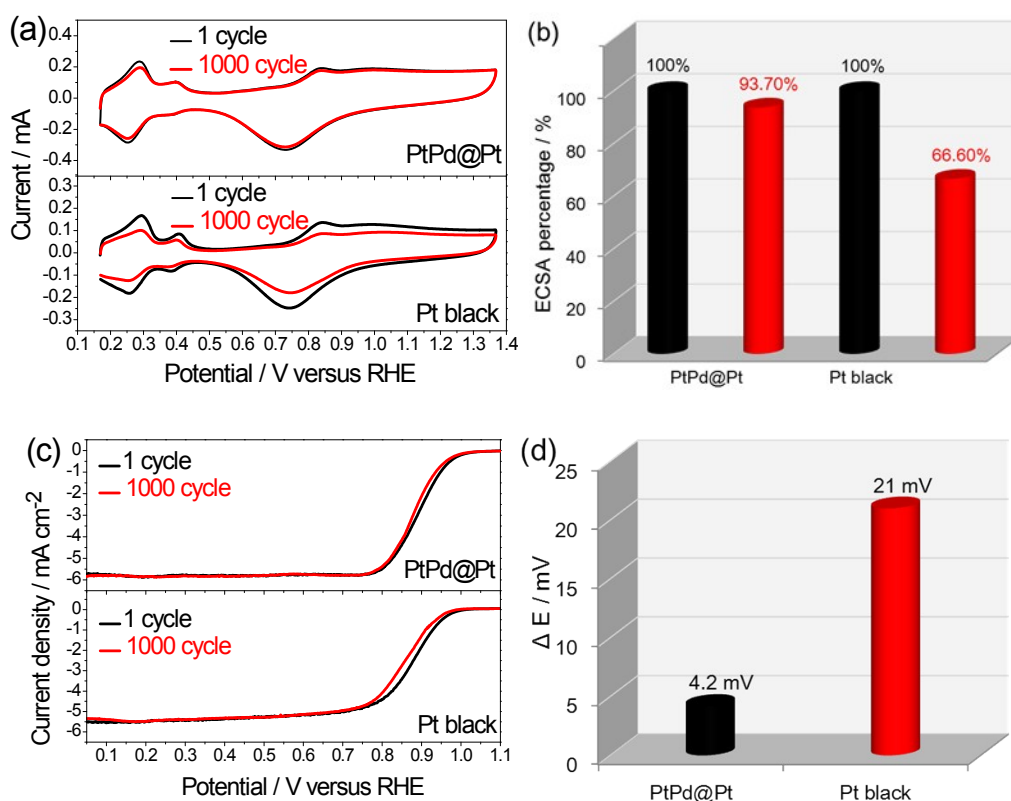


Figure S11. (a) CV curves of the PtPd@Pt nanoassemblies and Pt black before and after 1000 potential cycles in N_2 -saturated 0.1 M KOH solution at a sweep rate of 50 mV s^{-1} , and (b) the corresponding histogram of the ECSA degradation percentage before (black) and after (red) durability test. (c) ORR polarization curves of the PtPd@Pt nanoassemblies and Pt black before and after 1000 cycles in O_2 -saturated 0.1 M KOH solution at a sweep rate of 5 mV s^{-1} , and (d) the corresponding histogram of the degradation value in half-potential after durability test.

References

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